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THE USE OF LASER RAMAN SPECTROSCOPY FOR STUDY SEMICONDUCTOR FUNDAMENTAL PROPERTIES AND DIAGNOSTIC ANALYTICAL METHOD

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ABSTRACT. **In the present paper the use of a new direction-laser Raman spectroscopy first introduced in Georgia by the author for the purpose of studying semiconductor materials' fundamental properties is discussed. The importance of this direction and future trends of using it in other sciences is given in brief as well. The history and elements of theoretical principles are discussed shortly. The dynamics of technical evolution of Raman spectroscopy from early prismatic spectrometers with excitation of mercury lamps to modern laser Raman systems is given in chronological order. Within the limits of confined volume of the present paper I tried as far as possible to draw a clear picture of a single, double, triple Raman spectrometers and the function of systems and accessory combinations concerned with them; of advantage and expediency of their use in the various fields of scientific research. One of laser Raman systems constructed first by the author in Georgia, on which the experimental material has been performed is discussed in details. In the following two chapters the examples of using laser Raman spectroscopy in fields of studying and analyzing of semiconductor fundamental properties discussed in short are as follows: study of behavior of solid mixed semiconductors $ZnSe_xTe_{1-x}$, $GaAs_xP_{1-x}$; identification and quantitative analysis of ternary semiconductors GaAsP and GaAlAs synthesized during ion implantation of GaP and GaAs surfaces with phosphorous and aluminum.**

The invention of lasers, especially in visible area of spectrum, gave such a powerful incentive to renascence of Raman effect that it is difficult to find nowadays an advanced scientific center, which would not use laser Raman spectroscopy (LRS) in the field of investigation or analysis. For biologists and chemists this method has the same significance as infrared spectroscopy and even more informative in some cases. This time we consider the role of Raman spectroscopy in some areas of semiconductor study and only slightly touch upon an importance of using this method in chemical, biological, pharmaceutical and medical areas. Examples of using LRS in semiconductors will be presented in the given work on the basis of original works of the author.

When radiation passes through a transparent material, some part of the beam is scattered in all directions in this material. In 1928 the Indian physicist Raman revealed that the abovementioned part of scattered light differs from an incident beam. The mentioned part includes radiation of the wavelengths, which differ from incident wavelengths of excitation radiation. This shift of wavelengths depends on the structure of scattering molecule.

Today the theory of Raman scattering (RS) has been fully formed. It is stated that at RS the mechanism causing shifted wavelengths is the very quantum energetic levels as those at infrared (IR) absorption. That is the difference between excitation wavelength and those of scattered light corresponds to middle infrared area. Indeed, to compare RS and IR spectra for the same material, one can see similarity or identity. In brief, in IR spectroscopy those vibrations are active, whose molecular dipole moments alter according to vibrations; at RS those vibrations are active (becomes apparent in spectra), whose molecular polarization alters according to vibrations. Thus, RS and IR spectroscopy are not rivals, but mutually complementary from the point of view of information.

From the view of utilization in some cases to IR spectroscopy must be given priority, but sometimes RS is indispensable; thus, for example, when studying aqueous solutions. For RS experiments glass or quartz cuvettes are used; while in IR spectroscopy hygroscopic cuvettes made from alkali-haloid compounds are used, which are instable towards water and aggressive solutions. Thus, RS is of great importance in studying of biological and inorganic compounds and water pollutant objects. We shall not speak any more of more specific advantages of RS. We shall mention only a circumstance that sometimes hampers the use of RS. This is photoluminescence (PL) caused by impurities; though sometimes it is possible to avoid luminescence using corresponding experimental techniques.

A BRIEF THEORY OF RAMAN SCATTERING

To receive Raman spectrum (RS) the matter under study must be irradiated by laser intense monochromatic wavelength in ultraviolet, visible or near infrared regions of spectrum. During irradiation the scattered radiation must be measured by a corresponding spectrometer by a certain angle towards incident laser beam. In most cases this angle is 90°. In general Raman lines make 0.001% of intensity of excitation laser spectral line; as a result, detection and measurement of Raman spectrum is a complicated problem. This is no concern of resonance Raman scattering (RRS), Raman scattering enhanced by surface (SERS), resonance Raman scattering enhanced by surface (SERRS) and other effects of Raman scattering, which are characterized by much more powerful intensities. It should be underlined that today SERS is one of the powerful analytical methods for biologists, electrochemists and ecologists.

The scattered radiation is of three kinds, namely, Stokes, anti-Stokes and Relay radiations. The wavelength of the latter is the same as excitation laser wavelength and its intensity is far greater than two others. For example, Fig.1 shows Raman scattering spectrum for organic solvent CCl_4. To excite the spectrum, argon laser radiation of wavelength $\lambda_0 = 488.0$ nm, i.e. of wave number $\nu_0 = 20492$ sm^{-1} was utilized. In Fig.1 figures written above the peaks are Raman shifts calculated from the expression $\nu = (\nu_R - \nu_0)$ cm^{-1}. The Figure shows that a Raman spectrum is an aggregate of spectral lines positioned symmetrically to the right and left of the spectral line of an excitation laser. Anti-Stokes radiation is characterized by greater wave number than wave number of excitation line, while Stokes radiation peaks` wave numbers are less than that of excitation laser. It should be noted that Raman shift is identical for Stokes and anti-Stokes radiations. This shift is of the same value despite the fact with which laser wave number is being excited a RS spectrum of a given compound. Hence, Raman displacements of CCl_4 presented in the picture will be of the same value in spite of the fact, which laser -argon, krypton, YAG-Nd or helium-neon, will be used to record spectra.

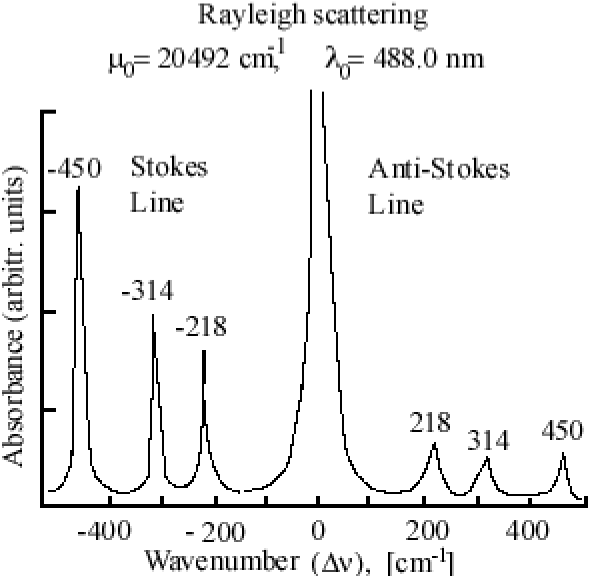

Fig.1. Raman scattering; relaxation spectrum of CCl_4

Anti-Stokes radiation is less in intensity in comparison with Stokes scattering and in practice in general only Stokes scattering is used while recording spectra. As for spectrum abscissa where Raman shifts are plotted, simply cm^{-1} are written instead of wave number. The sign minus is not written in case of Stokes scattering.

In usual or normal Raman spectroscopy excitation spectrally of a substance under investigation occurs with such a wavelength of laser radiation, which is far from any absorption peak of this substance.

Fig.2 shows Rayleigh and Raman (Stokes, anti-Stokes) scattering mechanism: the first thick arrow shows energy change in a molecule when it interacts with photons of an incident beam. Molecule energy increase is equal to photon energy *hv*. The second narrow arrow shows the change, which would be in case if a molecule met radiation when being on the first vibration level of the main electron state (as a rule only a few part of molecules are in such position). The two arrows in the middle part of the diagram show the changes causing Raleigh scattering. No energy loss takes place in this case because at Raleigh scattering elastic collision occur between a molecule and photon.

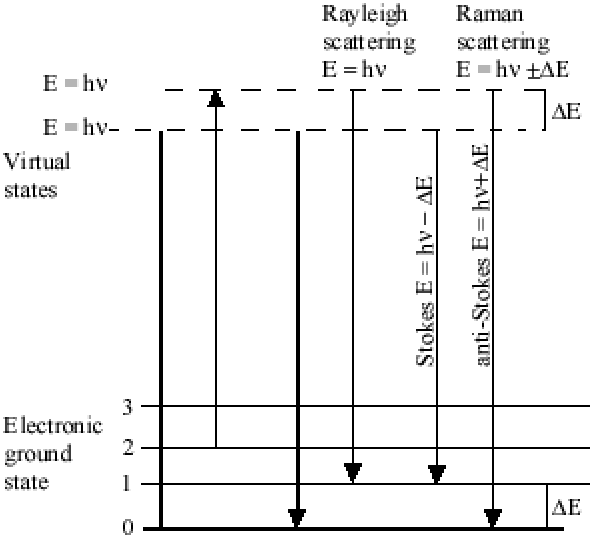

Fig.2. Relaxation of excited molecules and atoms

Energy change stimulating Stokes and anti-Stokes radiations as a result of inelastic scattering is presented on the right side of the scheme. The two latter radiations differ from Rayleigh scattering in frequencies corresponding to +ΔE energies, which are the first vibration level of the main electron state (if molecule bonds are active in IR region, then the energy absorbed by them will be +ΔE. Thus, Raman shift and IR-absorption peak frequencies will be the same).

The relative population of these two energy states is such, that Stokes scattering dominates over anti-Stokes. Besides, Rayleigh scattering is more probable than RS because energy transfer to molecule in the ground state and reemission by returning the same molecule to the ground state is more probable process. It should be noted that at room temperature the intensity of anti-Stokes spectral lines is weaker than that of Stokes. The reason is that in these circumstances only a few parts of molecules are in the first excited vibration state. The ratio of intensities of Stokes and anti-Stokes spectral lines is a function of compound temperature and increases with temperature.

As mentioned above, Raman effect is a very weak effect and its use in analytical way requires a great skill. This effect may be enhanced by a factor of 10^5 using RRS. Such enhancement is attained in case when the matter under consideration is being excited by laser beam with wavelength coinciding with some electronic transition of this matter. Regular RS and RRS are very often overlapped with photoluminescence, which is intensive by 10^7 than RS. For example, this occurs in case of excitation aromatic compounds with visible or ultraviolet lasers.

Fig.3 shows IR, Raleigh, RS, preresonance RS, RRS and the scheme of electronic and vibration terms of photoluminescence.

In Raman spectroscopy after recording Raman spectrum experimentally one must carry out certain calculations to go on from wavelengths received experimentally to Raman shifts expressed in cm^{-1}. For instance, utilizing popular argon green spectral line 514.5 cm^{-1} (more exactly 514.308 cm^{-1}) for excitation to receive Raman spectrum, wave number is calculated as follows:

$$\nu\lambda = 1/\lambda_0[nm]x10^7[nm]/[sm] = 1/514.308x10^7 = 19444 \ sm^{-1}$$

In this concrete case Raleigh scattering will take place at the same frequency, which has the green line of excitation argon and this frequency afterwards will be subtracted from all the scattered frequency, which will be fixed experimentally on the Stokes or anti-

Stokes side. One receives Raman spectrum with the abscess expressed in cm^{-1}, and ordinate-in scattered light intensities.

Reverse transfer is possible too; for example, if Raman peak is observed at 3000 cm^{-1}, the corresponding wavelength is calculated as follows:

$$\lambda_{RS} = 1/\nu_0 - \nu_{RS}[cm^{-1}]xE^7[nm]/[cm] = 1/19000-3000xE10^7 = 608.12 \text{ nm}$$

Thus excitation with green spectral line stimulates reemission of yellow spectral line in the result of Stokes scattering.

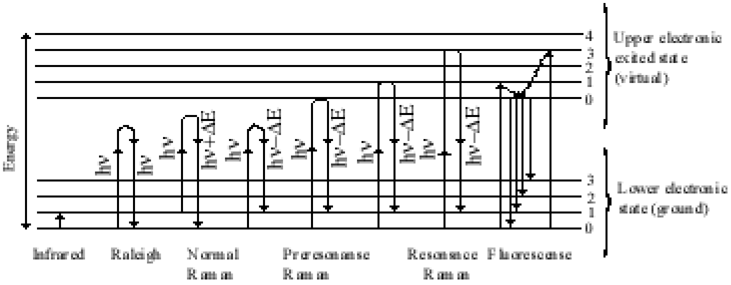

Fig.3. Relaxation patterns

It should be noted that those calculations are needed especially for home made, lab-type laser Raman-systems, as my laser-systems are. Modern expensive Raman spectrometers produced by foreign firms need not such manipulations due to complete automation and computerization.

EXPERIMENTAL LASER RAMAN SYSTEMS FOR RECORDING RAMAN SPECTRA FOR SOLIDS AND LIQUIDS

Nowadays there are foreign firms in the world, which put on sale laser Raman spectrometers of different category and function. These spectrometers are of different classes and their analytical or fundamental research possibilities are different. Recently almost all the firms produced Raman spectrometers, the price of which was about US $100000. There are today (and were) far expensive spectrometers. Just because of such a high price of those laser systems a lot of laboratories and researchers had to give up this method despite wish and necessity. Recently some firms in the world began to produce cheaper laser Raman spectrometers, especially for purpose of physical-chemical-pharmaceutical analyses. Such Raman systems cost about US $20000-30000. Perhaps these prices too are not available for most researchers, especially from such countries as Georgia.

A lot of researchers chose independent way to solve this problem -constructed a lab-type cheaper laser Raman-systems with semi-manufactured blocks.

According to the development of laser Raman-spectroscopy in Georgia and according to own scientific interests we too chose the same way.

Depending on the fact which semi-manufacture nomenclature is available it is possible to construct laser Raman-systems, which enables one to solve the scientific and analytical problems enclosed in the list of theoretical and practical ability of constructed laser Raman system.

We would like to share the experience with persons interested in, which they can use in their practical activity in case when their scientific or analytical activity demands using laser Raman spectroscopy and their financial means are not sufficient to purchase expensive laser Raman systems. It is necessary to add here that the same Raman-systems are fit for photoluminescence study too.

Any laser Raman-system consists of three main parts: exciting laser, single, double or triple spectrometer; sensitive signal detector with amplifier and registration systems. A container for specimen under consideration must be added to this complex, which gives us the possibility to study a specimen by various configurational scheme of Raman scattering. Besides these basic blocks, Raman spectrometer contains other accessories: optical, mechanical, cryogenic and other blocks or details.

Raman spectrometers depending on the basic principles of their construction are divided into some categories, which show the dynamics of LRS evolution. We do not touch on spectrometers with prisms as dispersion elements. They belong to history now. Though a good experimenter is able to use them to solve certain problems. The most widespread and integrated in laser epoch today is a double spectrometer with diffraction gratings, which are cut on lathe (replicas). The following stage of evolution is setting holographic gratings on double dispersion spectrometers; this gave experimenters opportunity to decrease sharply the quantity of stray light in spectrometers and get free from grating ghosts. Simultaneously the coefficient of light transfer decreased lightly in such spectrometers. The best triumph of Raman spectroscopy technique is considered thriple dispersion spectrometer with cut or holographic gratings set. These spectrometers are of specific importance to study such fine effects in semiconductors or in all other materials, which need to resolve spectral fine structure. After some time Raman spectrometer with Fourier Transform (FT-RS), semiconductor diode laser or YAG-Nd laser excitation was developed. This type of spectrometers has made revolution both in analytical and fundamental research area. The reason is that it is possible to record the spectra of such materials by this system, Raman spectra of which were impossible to record or were recorded by specially elaborated technique as these compounds, for example, aromatic compounds (petroleum, kerosene), dyes, impurities in semiconductors and etc., are luminescing strongly. It should be mentioned that in the former Soviet Union, the author of the given paper constructed the infrared Raman spectrometer with garnet laser excitation for the first time but on the basis of double diffraction (dispersion) spectrometer as early as in 1970 in Moscow Institute of Physics (FIAN) in collaboration with the laboratory of Academician Prokhorov. It was not a FT-RS but we have constructed it just to study luminescing narrowband semiconductors GaAs, InP, CdTe, narrowband mixed semiconductors obtained on basis of the mentioned semiconductors and impurities in semiconductors. In the last period from the time that holographic super notch filters' production achieved the highest level, laser Raman systems with set of single diffraction spectrometer and holographic notch filters sat on sale in international spectroscopic market. Such Raman systems are far small in volume, light, comparatively cheap and for fulfillment of certain tasks have some advantages even over a triple Raman spectrometer. In this system the notch filter serves as the first stage monochromator and in case of a good super notch filter it is possible to approach the exciting laser wavelength by 100cm^{-1}. In triple spectrometer this value is about 10 cm^{-1}, but in turn, the coefficient of light transfer is far great for a single spectrometer. A novelty in Raman spectroscopy, which is conveyed by the use of CCD detectors as detectors should be underlined specially. In such complex instead of a spectrometer a spectrograph is used and laser Raman system becomes multi-channel device. With such configuration sensitivity increases many times, which has resolving practical importance in analytical sciences.

So, the criteria for purchase or construction a spectrometer type is based on the target of the task. There is a better variant too: if one has 1500000 (perhaps it will not suffice), it is possible to purchase several Raman systems of various types and then purposes of a problem will not be confined. These are the basic types of Raman systems, which exist nowadays. We do not touch on a lot of branches and details. Now we present a model and a brief description of one of the laser Raman systems, which we have constructed first in Georgia and carried out investigation of some semiconductor materials.

Table 1

The laser wavelength, corresponding to quantum energies and types used by us

Lasers	Laser Type	Wavelength (nm)	Energy (eV)
He-Ne	gas	632.8	1.958
Argon ion	gas	514.5 501.7 496.5 488.0 476.5 457.9	2.408 2.469 2.495 2.539 2.600 2.705

Cripton ion	gas	647.1 568.2 530.9 520.8 476.2	1.914 2.180 2.33 2.379 2.601
He-Cd	gas	441.7	2.805
Copper	metal vapour	510.6 578.2	2.428 2.144
YAG:Nd	solid	1064.0	1.17
Die	solution	540.0-690.0	2.296-1.797

Fig.4 shows the scheme of a laser Raman system constructed by us. The exciting source is argon, krypton, helium-neon, helium-cadmium, cuprum lasers. Those wavelength, which characterize the abovementioned lasers' radiation and we use for Raman spectra excitation, are given in Table 1. These lasers mainly are of standard, fabric production. At the same time we have also home made laboratory type lasers as follows: krypton and argon lasers. Argon and krypton lasers constructed by us have the following parameters: krypton laser radiation is single-mode with wavelengths 530.9, 568.2, 647.1 nm, integral power about two watt, with vertical polarization radiation. Argon laser is characterized with the following parameters: single-mode, with wavelength of radiation 457.9, 476.5, 488.0 496.5, 501.7, 514.5 nm; at integral power about 3 Wt, vertically polarized radiation. Argon and krypton lasers of laboratory types constructed by us enable us to vary widely experimental conditions. This circumstance is promoted by the fact, that two high voltage rectifiers of laser active element and magnetic solenoid constructed by us work autonomicaly in current change mode.

To obtain spectra we use double diffraction spectrometer DFS-24, with diffraction replica 1200 str/mm. For these gratings the maximum concentration of light comes about on yellow region of spectra; therefore there are optimal conditions to receive Raman spectra for some of excitation wavelengths of lasers used by us, whereas for others there is a compromise situation.

To create optimal conditions for all the laser excitation wavelengths we have constructed three various types of Raman spectrometers in correlation with radiation of lasers exciting the optical system. We are not going to speak of these systems.

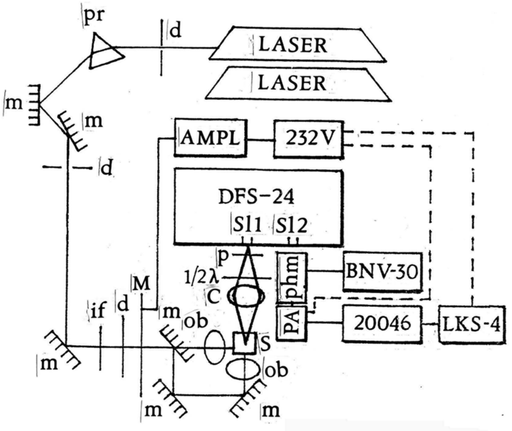

Fig.4. General scheme of home-made laser Raman-system constructed by us

Laser emission through diaphragm (d), prism (p), interference filter (if), mirrors (m) and objective (ob) is filtered from laser background, plasma lines; highly collimated monochromatic emission in desired direction is formed according to planned scattering configuration focusing on the semiconductor (s) to be studied. Irradiation scattered in the semiconductor is collected by the condenser (c) and through the polarizator (p) is focused on the monochromator entrance slit (sl.1). Photoluminescence or Raman scattering signal from the exit slit (sl.2) falls on the photomultiplier (phm) and after amplifying and sorting photoluminescence or Raman scattering spectra are recorded by the recorder LKS-004. Detection and amplification signals of weak intensity of Raman scattering is done by two methods: a) synchronous detection-with the aid of modulator and lock-in-amplifier Uniphan 232B; or b) photon counting-with the aid of radiometer 20046.

In the visible area we use photomultiplier FEU-79 or FEU-136 with well-selected parameters. In case of need cathode of FEU-79 is cooled at about -100^0 C. Towards this purpose we have constructed low-temperature cryostats of three different types working on different principles. By cooling cathodes of FEU-79 in these cryostats we are able to increase noise to signal ratio nearly to eight which is of great importance when registering Raman-spectra.

Besides abovementioned laser Raman spectroscopy we have constructed low temperature cryostats of various types and construction, which give possibility to study PL and Raman spectra at nitrogen and helium temperatures both in fixed temperature and temperature change mode. These optical compact cryostats we have created especially for Raman spectroscopic investigations taking into consideration that in the process of RS measurements direction of excitation laser beam, crystallographic axis of specimen under investigation-semiconductor and collection angle of scattered radiation form differed configurations in various configuration schemes of measuring.

To study the effect of pressure having a uniaxial direction on Raman spectra of semiconductors and PL, we have constructed a special cryostat for our Raman systems, which works at nitrogen temperature.

Besides low temperature cryostats, we have constructed also a high temperature cryostat, which gives us the possibility to study semiconductors from 18^0C to 600^0C.

Thus, the Raman system we have constructed enables us to carry out large-scale fundamental research of solids (crystals, mixed solid solutions, amorphous, glass, pouders, small crystals, fine-dyspersated materials) and analytical works with very wide scale of spectral excitations, under influence of stress having a uniaxial direction and in the range of temperature from 10^0K to 300^0K. These investigations may be conducted both on transparent crystals and thin films.

It should be noted that the described system enables one to carry out investigations and analytical works in Raman spectroscopy on liquids as well, which chemists, biologists, pharmaceutics, medics, agricultural workers, geologists, etc are interested in.

In the following part of this paper the experimental material, which we have done on abovementioned Raman systems in some brunch of semiconductor study is discussed.

RAMAN SPECTROSCOPY OF MIXED SEMICONDUCTORS

Mixed crystals are one of basic materials of semiconductor microelectronic devices. For instance, light emitting diodes and laser diodes are being prepared on their basis. The main criteria of utilizing of such materials is that that all their physical chemical properties depends upon their composition; hence one can prepare devices with previously planned properties on their basis. The main property possibly is the dependence of forbidden band on composition.

The first mixed crystals complex we have studied is GaAsP from A^3B^5 group known in optoelectronic instrument making. As it is known, on the basis of this material light emitting diodes of a good quality in red, orange and yellow spectral ranges are being prepared. Laser diodes are prepared in the same manner. These materials were studied earlier by laser Raman spectroscopy [1]. In the mentioned paper these materials were investigated by volume excitation, with 632.8 nm of helium-neon laser and 106.0 nm of garnet laser radiations. It should be noted one of the most important methodical circumstances in Raman spectroscopy: when such semiconductor as GaAs (it is one of components of crystals under observation), is studied with RS, the spectrum of plazmon-phonon interaction is added to phonon spectrum. Plazmon influence on phonon spectrum is more when excitation is bulk and electroactive impurities are in great quantity in semiconductors (the quantity of free electrons is great). We have studied three epitaxial films of various compositions, exactly such films, on the basis of which light emitting diodes are produced in the abovementioned three spectral ranges. Thus, concentration of electrons in these films is great, about 10^{19} cm^{-3} orders. Because of this we studied these films by surface reflection method with argon laser excitation with 488.0 nm radiation. In such experimental conditions we are far from interfering photoluminescence. Besides, as 488.0 nm radiation penetration skin-layer is small in mixed crystals under research, about 150.0 nm, plazmon influence on phonon spectrum is less. Thus, we have the possibility to study these crystals in natural conditions with relations to diagnostics and at the same time to decrease eminently or annihilate interfering factors, which are characterizing bulk excitation.

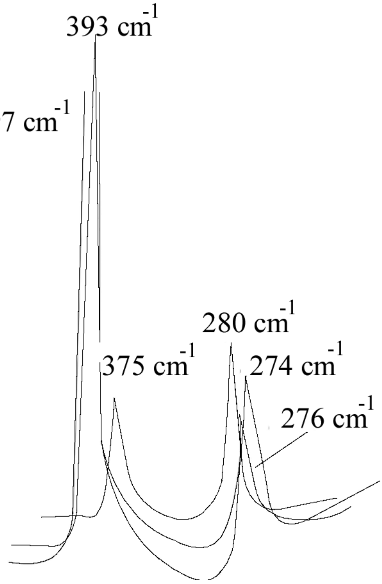

Fig.5. RS spectra of $GaAs_{0.6}P_{0.4}$, $GaAs_{0.35}P_{0.65}$ and Ga $As_{0.15}P_{0.85}$; $\lambda_L = 488.0$ nm

The mixed crystals $Ga_xAs_{1-x}P$, which have been studied, are epitaxial films. These films are grown epitaxially on GaP substrate of (001) orientation. Fig.5 shows RS spectra of GaAs, $GaAs_{0.6}P_{0.4}$, $GaAs_{0.35}P_{0.65}$, Ga $As_{0.15}P_{0.85}$ and GaP. For excitation of these spectra we have used argon laser radiation of wavelength 488.0 nm.

All crystals under investigation are of cubic symmetry and belong to T_d point symmetry. Therefore, according to selection rules only LO phonons must be active in Raman spectra of the studied surface (001).

The spectra in Fig.5 prove this. The figure shows that in Raman spectra of mixed films two categories of LO phonons are observed- LO_1 and LO_2 in contrast to GaAs and GaP. The first, LO_1 shows longitudinal vibrations of atoms of GaAs-like sublattice, and the second, LO_2 shows longitudinal vibrations of atoms of GaP-like sublattice. Table 3 shows the frequencies of observed phonons. On base of these data the schemes in Fig.6 are plotted, which show dependence of composition of this mixed semiconductor on longitudinal phonon frequencies.

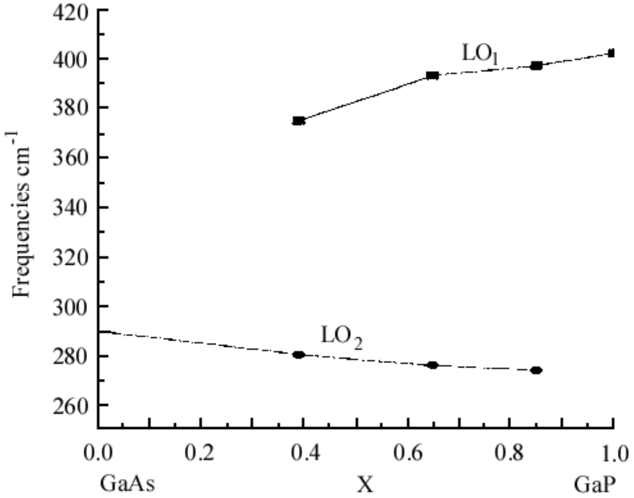

Fig.6. Dependence of composition x of mixed semiconductors $GaAs_sP_{1-x}$ on longitudinal phonon frequencies

Table 2

Semiconductors	LO_1 (cm^{-1})	LO_2 (cm^{-1})

GaP		402
$GaP_{0.85}As_{0.15}$	274	397
$GaP_{0.65}As_{0.35}$	276	393
$GaP_{0.39}As_{0.61}$	280	375
GaAs	290	

It is known that mixed crystals according to their behavior are divided into two classes [2]: single-mode behavior and two-mode behavior. The dependences presented in Fig.6 show that mixed crystal $GaAs_xP_{1-x}$ belongs to two-mode crystals. These graphics work for estimation of unknown concentrations. We shall illustrate this later, when we touch the problem of RS study in semiconductors modified by ion implantation.

The second system of mixed crystals, which we have studied, is A^2B^6 group semiconductor $ZnSe_xTe_{1-x}$. The system we have studied is bulk crystal. They are cut as cubes and all faces of the cube are optically polished. The crystals are polycrystalline and orienting of these crystals has not been carried out. Because of this it is impossible to hold forbidden law in RS spectra; hence, when recording spectra we are not able to separate LO and TO phonons as we did in the previous case.

To obtain Raman spectra of this system we used almost volume excitation of krypton laser radiation of 568.2 nm wavelength (2.18 eV). Simultaneously we recorded spectra with helium-neon laser radiation of 632.8 nm wavelength (1.98 eV); this is far away from forbidden gap value of semiconductors under investigation. In this case RRS is eliminated for all compositions. But when exciting by krypton laser we create preresonance conditions during recording spectrum for pure ZnTe. This system never has been investigated in such conditions. To clarify our argumentation, we present Fig.7, which shows the dependence of composition x of this system upon forbidden gap magnitude E_0 [3]. As it is seen, the dependence has a minimum. Because of this for this compositions krypton laser quantum energy 2.18 eV is more than forbidden band width for compositions near minimum, while ZnTe and some compositions are fully transparent for this radiation. To create more equal conditions, for exciting the spectra we have used radiation wavelength of dye laser 589.8 nm (2.102 eV). Fig.8 shows two Raman spectra of ZnTe: one 632.8 nm and the second wavelength excitations 589.8 nm. The spectra show clearly the distinction: in spectra recorded in resonance conditions we were able to fix multiple 2LO phonons. One cannot attain this by increasing intensity of radiation of helium-neon laser or spectrometer sensibility, because revelation of multiple phonons lays in physical mechanism in this case. This mechanism is phonon cascade mechanism and its realization occurs when excitation laser quantum energy and semiconductor forbidden gap width achieve a certain ratio. At this time preresonance or resonance situation takes place, but it is impossible to detect this effect in all types of semiconductors. Fig.9 shows Raman spectra of mixed crystals we have studied, when excitation occurred by 589.8 nm wavelength of dye laser radiation. Table 3 shows the observed phonon frequencies. On the basis of these data we have plotted LO, TO and 2LO phonons' concentration dependence (Fig.10). The graphs differ diametrically from schemes discussed and studied at first. The schemes for the second system show that the system $ZnTe_xTe_{1-x}$ belongs to single-mode behavior crystals.

Table 3

Semiconductor composition x	**LO (cm^{-1})**	**TO (cm^{-1})**	**2LO (cm^{-1})**
ZnTe	203	170.7	409.5
$ZnTe_{0.9}Se_{0.1}$	207.3	173.5	415
$ZnTe_{0.8}Se_{0.2}$	210	176	423.2
$ZnTe_{0.7}Se_{0.3}$	215.7	177	436.9
$ZnTe_{0.6}Se_{0.4}$	221.3	179.7	450.5
ZnSe	250	205	

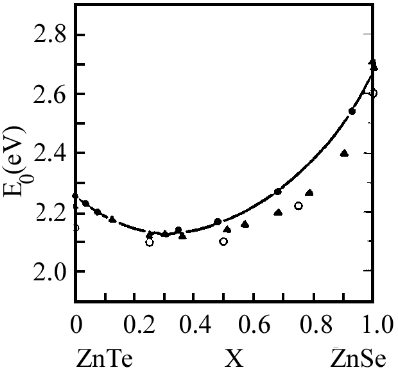

Fig.7. Lowest band gap E_0 of $ZnSe_xTe_{1-x}$ as a function of x at room temperature

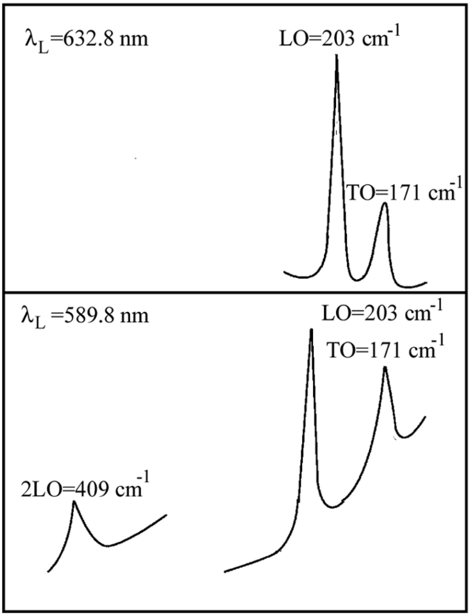

Fig.8. Raman spectra of ZnTe a-λ = 632.8nm and b-λ = 589.8nm excitation

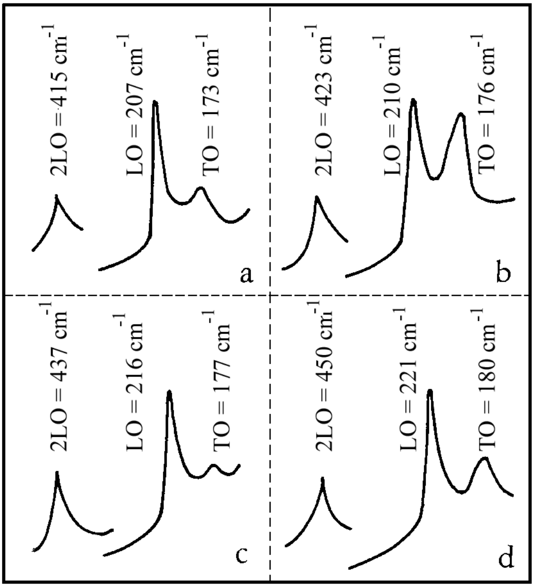

Fig.9. Raman spectra of mixed crystals a-$ZnSe_{0.9}Te_{0.1}$; b-$ZnSe_{0.8}Te_{0.2}$; c-$ZnSe_{0.7}Te_{0.3}$; d-$ZnSe_{0.6}Te_{0.4}$; λ_L=589.8nm

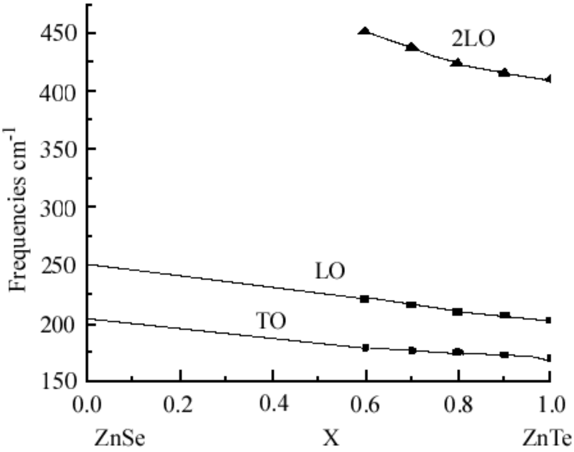

Fig.10. Dependence of composition x of mixed semiconductors $ZnSe_xTe_{1-x}$ on LO, TO and 2LO phonon frequencies

In this case at single-mode behavior characteristic phonons LO, TO and 2LO of mixed semiconductors change monotonously according to composition; two-mode crystals' characteristic property consists in formation of local or gap vibrations and therefore in graphical form of other type. This was illustrated in the process of study of the first system.

RAMAN SPECTROSCOPY STUDY OF SEMICONDUCTORS MODIFIED BY ION IMPLANTATION

Ion implantation is one of the actual methods of modern semiconductor complex micro technology; at present the fabrication of a device occurs rare without this method. Nowadays a lot of physical diagnostics are elaborated for monitoring of ion implanted surfaces and Raman spectroscopy is one of leadings among them.

We present here only a part of experiments carried out in this direction and it concerns synthesizing of ternary mixed crystals by ion implantation technology and then identification-diagnostics of such systems by Raman spectroscopy.

At synthesizing of compounds by ion implantation a lot of radiation defects as well as amorphous phase are formed. That is why high temperature annealing in high vacuum or inert gas atmosphere is necessary afterwards to receive crystalline phase. The ternary semiconductor $GaAs_xP_{1-x}$ synthesized by ion implantation was first studied with laser Raman spectroscopy by us [4]. Almost simultaneously the similar study of the question was presented in [5]. According to the authors of the above-mentioned work the ternary compound crystal phase is obtained directly during the so-called hot implantation and no further heat treatment is necessary in this case.

The aim of the work presented here is to study the technological conditions of synthesizing by ion implantation of crystalline mixed ternary semiconductors $GaAs_xP_{1-x}$ and $Ga_xAl_{1-x}As$ using laser RS.

We implanted polish surfaces of GaAs with 70 KeV phosphorous and 100 KeV aluminum ions, with $1.8x10^{17}$ ion/cm^2 and $2.8x10^{16}$ ion/cm^2 doses. The orientations of surfaces were (111) in the first case and (001) in the second relatively. GaAs substrate was located at the room temperature at the time of phosphorous implantation and at 400° C at the time of aluminum ion implantation.

As we showed in [6], single-phase amorphous ternary semiconductor α–$GaAs_xP_{1-x}$ is formed when implanting GaAs by phosphorous at room temperature. The amorphous phase is formed during the hot implantation too, when implanting at 450^0C. Fig.11 shows Raman-spectra of standard GaAs of (111) orientation and of α-GaAsP formed by phosphorous implantation. According to the selection rules LO phonon characteristic peak is seen in the Raman-spectra of the crystalline GaAs at 290 cm $^{-1}$ frequency and TO phonon characteristic peak at 268 cm^{-1}. While amorphous compound Raman-spectra are characterized by two wide bands: one corresponds to Ga-As bond vibration and the second-to Ga-P bond vibration.

We used the thermal annealing in the high vacuum to recover the crystal structure. Before annealing we coated the surface of implanted GaAs with about 1000 A thickness protective layer of SiO_2 to avoid the phosphorous and arsenic evaporation from the crystalline surface. We carried out annealing at 500, 700 and 850^0 C during an hour. The general picture of Raman spectra recorded after annealing at the above temperatures, is represented in Fig.12. It is clearly seen that as a result of annealing, α-$GaAs_xP_{1-x}$ transforms gradually into a crystalline state and at the 850^o C nearly entirely recovering of crystalline phase takes place, although a small amount of radiation defects is still felt. This fact is confirmed by narrowing of wide bands typical for amorphous phase with rising of annealing temperature and formation of new peaks at 370 cm^{-1} and 345 cm^{-1} frequencies, respectively. We referred these peaks to LO_2 and TO_2 phonons vibration of ternary compound GaAsP.

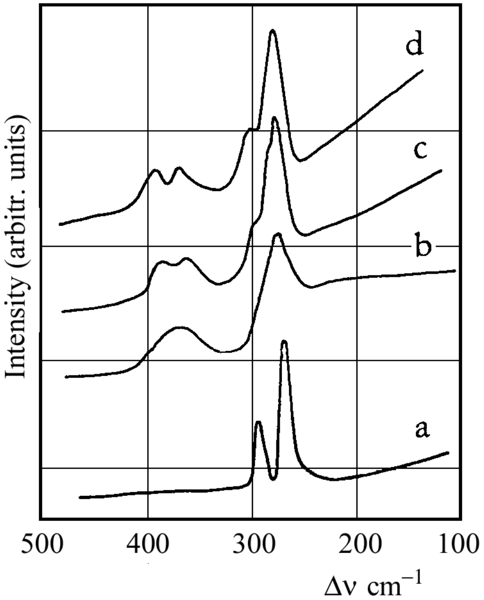

Fig.12. Raman spectra indicating the crystallization process of α-GaAsP: a-the spectrum of the standard GaAs with orientation (111); b, c, d-the spectra of crystals received after quenching at 500, 700, 850^{0}C, respectively

The synthesizing of the mentioned ternary compound is confirmed by formation of a peak at the 278 cm $^{-1}$ shifted by 12 cm^{-1} from the LO phonon of the standard GaAs. This peak relates to the LO$_1$ phonon vibration of the synthesized crystalline GaAsP.

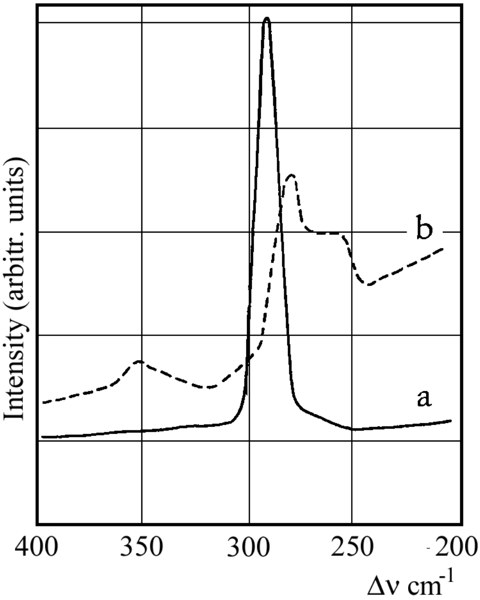

Fig.13. Raman spectra of the standard GaAs with (001) orientation (a) and α-GaAlAs (b) formed by aluminum hot implantation

Fig.13 shows Raman-spectrum of (001) oriented GaAs before implantation and after hot implantation of aluminum. According to the selection rule only the peak at 290 cm^{-1} corresponding to the LO phonon is observed in the Raman-spectrum of (001) oriented surface of GaAs. While after aluminum implantation as it is seen from the picture the sharp peak corresponding to the LO phonon disappears and a wide spectral band is formed which reflects the vibration of Ga-As bond; simultaneously near 360 cm^{-1} a wide band of low intensity is formed which reflects the Al-As bond vibration. The two experimental facts indicate that amorphous α-Ga_xAl_{1-x} is formed at the hot implantation too. Besides the Raman-spectra show that a low-intensity sharp peak is formed at 284 cm^{-1}, which is shifted from the LO phonons of the crystalline GaAs by 6 cm^{-1}. Therefore the peak corresponds to the low amount of crystalline GaAlAs formed due to the hot implantation. Thus at the hot implantation of GaAs, α-GaAlAs is formed together with a few amount of crystalline phase.

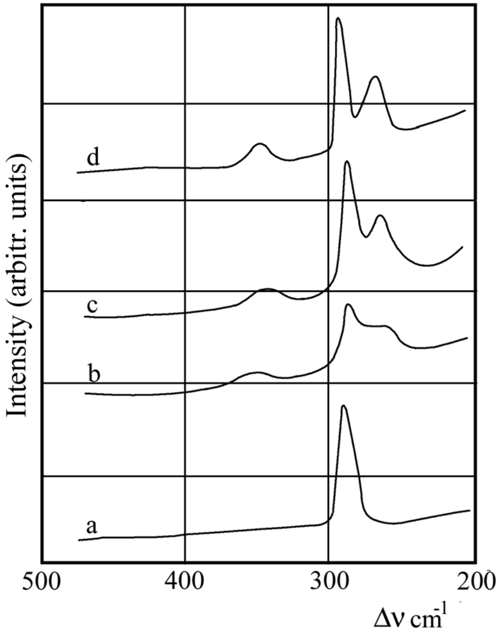

Fig.14. Raman spectra indicating the crystallization process of α-GaAlAs: (a) the spectrum of standard GaAs with (001) orientation; (b) the spectrum of α-GaAlAs synthesized by hot aluminum implantation; (c,d) the spectra of crystals received after quenching at 500, 700^{0}C, respectively

In this case just as in the case of phosphorous implantation for crystal lattice recovering we have used high-temperature annealing in vacuum at 500, 700 and 850^{o}C. The Raman-spectra reflecting the received results are presented in Fig.14. It is seen that at 500^{0}C annealing characteristic wide band of α-$Ga_xAl_{1-x}As$ is sharply splitting into two narrow peaks with frequencies 281 cm^{-1} and 263 cm^{-1} respectively. These frequencies are shifted by 6 cm^{-1} and 5 cm^{-1} from the characteristic frequencies of LO and TO phonons of standard GaAs, they characterize the vibration of GaAs sublattice of crystalline GaAlAs and belong to the LO_1 and TO_1 phonons, respectively. In the same time a new peak formation occurs at 360 cm^{-1} which we ascribe to the AlAs sublattice vibration in the crystalline GaAlAs that is expressed by LO_2 phonon. When annealing at 700 and 850^0 the crystalline phase of GaAlAs becomes more and more perfect because of disappearance of radiation defects. This is clearly reflected by a sharp increase of intensity of peaks characterizing LO_1, TO_1 and LO_2 phonons and by narrowing their half-width with the increase of the annealing temperature.

As it is known from the experiment conditions, the GaAs substrate orientation was (001) and therefore only LO phonon was observed in the Raman-spectrum. But in the Raman-spectra of the ternary compound GalAs synthesized after implantation and annealing LO_1 and LO_2 phonons as well as TO phonon are observed. At the same time the spectra show that the TO_1 phonon intensity is much more less than LO_1 phonon intensity. Therefore one can conclude that the crystalline lattice of the ternary compound recovered due to annealing is polycrystalline. At any rate it does not repeat the substrate orientation (001).

Thus, in the result of phosphorous and aluminum implantation of GaAs with subsequent high temperature annealing in the vacuum crystalline ternary compounds of GaAsP and GaAlAs are synthesized. We have stated, that the perfect crystalline phases of the mentioned compounds are got as a result of subsequent thermal treatment regardless of the fact at what temperature the ion implantation occurrs, at room or high temperature.

Thus, it is clear from this work how multiform and interesting is the utiliziation laser Raman spectroscopy in semiconductor science of materials and microelectronics dealing with study of fundamental properties as well as analysis.

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